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Triphenylamine-Based Open and Macrocyclic Receptors: A Study Towards Selectivite Recognition of Aliphatic Dicarboxylates

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Triphenylamine-based fluorescent open and macrocyclic receptors **1** and **2** have been designed and synthesized for the recognition of linear aliphatic dicarboxylates of varying chain lengths. *o*-Phenylenediamine in the form of an amide has been utilized as the binder of carboxylate. The binding behavior was studied in polar solvents using ^{1}H NMR, fluorescence and UV-vis spectroscopic methods. Binding takes place at the charge neutral binding sites of the receptors with concomitant change in emission. The open structure **1** exhibited selectivity for long chain dicarboxylates while good selectivity for glutarate was achieved in the case of macrocycle **2.**Theoretical studies on both **1** and **2** itself and their complexes with dicarboxylates have been done in details.

Introduction

Over the past several decades, considerable effort has been invested to the development of small molecule anion receptors that are capable of binding anionic species with high affinity and high selectivity. This has been driven due to numerous roles played by anions in biological, environmental and chemical sciences.[1]Dicarboxylates are important class of biologically relevant anions that are involved in various metabolic pathways such as kreb's cycle, fatty acid metabolism etc.[2] Therefore, examination of these substrates in biological fluids (e.g., urine, blood etc.) offer valuable information for the diagnosis of metabolic disorder and neurological diseases. Dicarboxylates are also important component in atmospheric aerosol and acts as cloud condensing nuclei thereby influences earth's radiative forcing and climate.[3] Owing to such biological, medicinal and environmental significances, synthetic receptors capable of recognition and sensing dicarboxylates are highly desirable. In this regard, fluorescence sensory system finds considerable attention due its simplicity and high sensitivity for the visualization of target analytes.[4]

Selective recognition of anions is often constrained by the diverse geometry, low charge to radius ratios, high solvation energy and narrow pH-window. In particular, recognition of dicarboxylate anion is even more challenging than inorganic anions, due to high hydration energy and wide variety in sizes and conformations of the dicarboxylates. Therefore, effective complexation could only be achieved by proper installation of recognition site in the binding domain forming a large cavity of suitable topology to accommodate dicarboxylate of particular size or geometry. There have been numerous reports that take advantage of binding sites such as ammonium, guanidinium, imidazolium, pyridinium, urea/thiourea, amide groups and metal ions for the effective complexation with dicarboxylate guests.[5] In this regard, polyammonium group- containing receptors have been utilised most successfully for dicarboxylate binding because it can interact *via* both electrostatic and hydrogen bonding interactions. However, their usefulness is constrained by the fact that ammonium group exists in acidic medium while dicarboxylates generally exist as dianionic species above and around pH 7. Although a large number of neutral receptors have been synthesized for dicarboxylates, only few fluorescent receptors that could discriminate various linear aliphatic dicarboxylates are known,[6] and systems that could selectively recognize desired dicarboxylate remain a challenge.

The propeller-shaped triphenylamine (TPA) platform could serve as an excellent fluorescent probe in reporting recognition events, and various modified TPA-systems have been reported by us and other groups.[7] Herein we report our endeavour on the design and synthesis of TPA-based receptors **1** and **2** for recognition and sensing of aliphatic dicarboxylates of various chain lengths.

Although the acyclic receptor **1** efficiently binds long chain dicarboxylate (glutarate, adipate, pimelate and suberate), the relevant differentiation in the stability of the complexes is less. On the other hand, the macrocyclic receptor **2** displayed high

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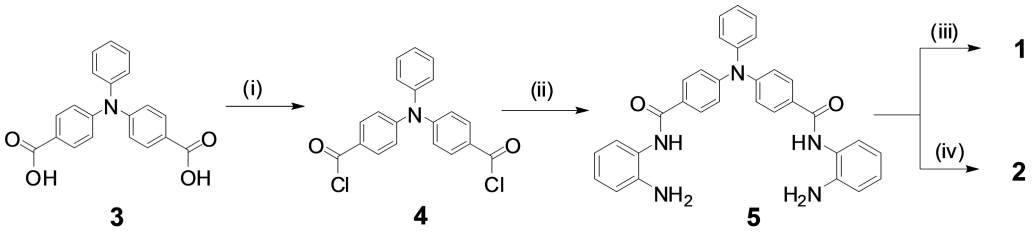

Scheme 1. *Reagents and conditions:* (i) Oxalyl chloride, DMF, dry DCM, 15 h; (ii) *o*-phenylenediamine,Et_3N/dry DCM, 8 h; (iii) Butyryl chloride,Et_3N, dry THF, 6 h; (iv) Adipoyl chloride,Et_3N, dry THF, high dilution, 2 days.

selectivity toward glutarate over the other aliphatic dicarboxylates studied. *Ortho*-phenylenediamine-based diamide has been exploited for hydrogen bonding interaction with anionic dicaboxylates. The peripherally substituted binding sites are expected to modulate the electron density of the TPA moiety. The hydrogen bonding pattern of the different binding sites is expected to alter the excited state properties of the receptor by changing the angle around the central nitrogen. As detailed below, this outcome has indeed been achieved.

Results and discussion

The syntheses of receptors **1** and **2** are outlined in Scheme 1. It starts with triphenylamine dicarboxylic acid **3**, which was synthesized using reported procedure.[7d] Compound **3** was first treated with oxalyl chloride in dry CH_2Cl_2 in the presence of catalytic amount of DMF to afford the diacid chloride **4** which on subsequent reaction with excess *o*-phenylenediamine gave the diamine **5.** Reaction of **5** with butyryl chloride afforded the receptor **1** in 79% yield. High dilution coupling of **5** with adipoyl chloride in dry THF gave the macrocycle **2.** All the compounds were characterized by standard spectroscopic techniques.

Initial evidence that the receptors **1** and **2** could bind aliphatic dicarboxylates in solution came from ^{1}H NMR spectroscopic analyses carried out in DMSO-d_6 solution. The proton resonances at 9.79 ppm and 9.67 ppm for **1** and at 9.92 ppm and 9.38 ppm for **2** were assigned to amide NH_a and NH_b protons, respectively. Upon addition of equivalent amounts of different dicarboxylates (as their tetrabutylammonium salts) to DMSO-d_6 solution of the receptors, amide proton resonances shifted to the downfield directions ($\Delta\delta_{NHa}$ = 0.00 - 1.61 and $\Delta\delta_{NHb}$ = 0.12 - 1.67 for receptor **1** and $\Delta\delta_{NHa}$ = 0.01 - 1.33 and $\Delta\delta_{NHb}$ = 0.01 - 1.22 for receptor **2**). This is consistent with the formation of hydrogen bonding complexes between the anionic guests and the receptors in polar solvent. The fact that the extent of downfield chemical shift of the amide protons of the receptors was different for different dicarboxylates indicates their differential affinity for the binding site (Table 1S). It is also worthy to note that DMSO being a competitive solvent reduces the interaction between the host and guest. In some cases, upon complexation, the signals for the phenyl ring protons around the central nitrogen of the TPA core were resolved to a significant extent. This led us to conclude that complexation is accompanied by a conformational change of the TPA core around the central nitrogen atom. This was further supported by theoretical calculations as described below.

In order to asses the sensing properties of the receptors **1** and **2**, fluorescence and UV-visible titrations were performed in CH_3CN containing 0.4 - 2% DMSO (DMSO was used to make the solution homogeneous). Upon addition of the dicarboxylates to the receptor solution of **1**, discernible change in emmision intensity with no appreciable shift in the emission maximum (λ_{max} = 444 nm following excitation at 350 nm) was noticed (Figure 2 and Figure 9S). Figure 2B shows the change

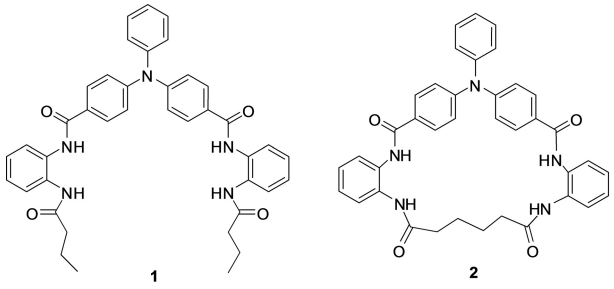

Figure 1. Receptor structures of **1** and **2.**

in fluorescence intensity of **1** in the presence of dicarboxylates of various chain lengths. It is evident from Figure 2B that long chain dicarboxylates such as pimelate and suberate (Figure 2 A) perturb the emission of TPA motif significantly compared to the short chain analogues. When exposed to malonate, negligible change in fluorescence emission of **1** was observed. This is presumably due to the poor association of malonate with the binding cleft of **1.** For all anions, except adipate, the emission of **1** was reduced by different amounts. The binding induced quenching of emission may be attrubuted to the activation of PET (photo induced electron transfer) process occuring between the binding site and excited state of TPA moiety (Figure. 18S). The increase in emission of **1** in the presence of adipate is presumably attributed to the change in the positions of the molecular orbitals of the conformationally mobile TPA unit.

In contrast to what is seen in the case of **1**, when a flexible adipoyl spacer in the macrocycle **2** connects two *o*-phenylenediamine binding sites of the two arms, glutarate selective quenching of emission is observed (Figure 3 and Figure 10S). The short chain dicarboxylate malonate and succinate perturbed the emission of **2** moderately while long chain dicarboxylates such as adipate, pimelate and suberate induced negligibly small change in emission. This led us to conclude

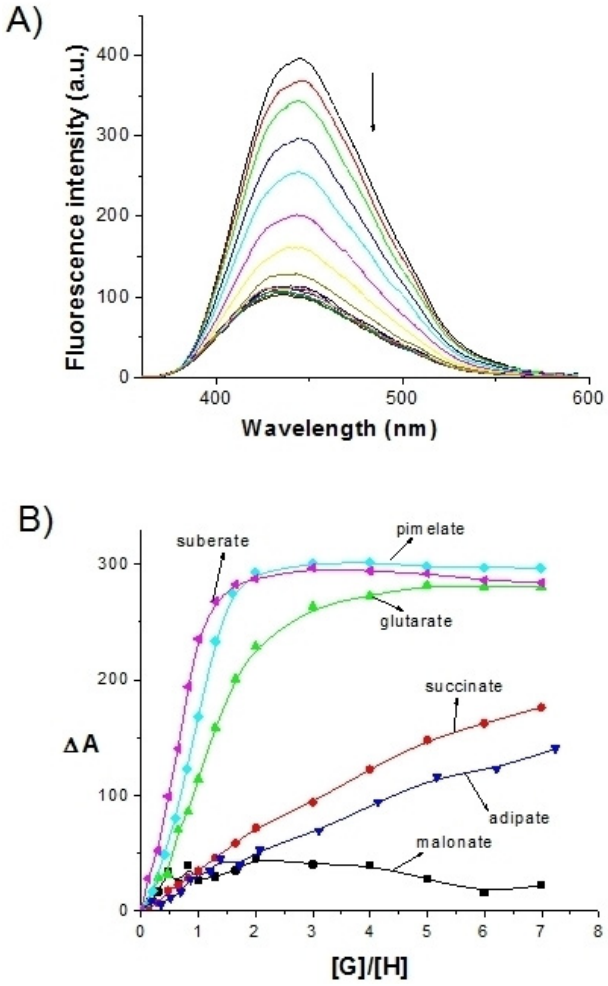

Figure 2. A) Change in fluorescence intensity of **1** ($c = 7.66 \times 10^{-5}$ M in CH_3CN containing 0.4% DMSO) upon addition of suberate ($\lambda_{max} = 444$ nm); B) Titration curves of receptor **1** ($c = 7.66 \times 10^{-5}$ M in CH_3CN containing 0.4% DMSO) from fluorescence study (measured at 350 nm).

that glutarate is the right size for binding optimally within the cavity and thus quenches the emission of **2** dramatically compared to other dicarboxylates of higher and lower chain lengths. As in the case of **1**, the anion induced quenching of emission of **2** is ascribed to the activation of PET process occurring during complexation (Figure 18S). Importantly, the degree of quenching of emission in each receptor varied with the chain length of the dicarboxylates.

To provide more insight into the sensitivity and selectivity of the host-guest interactions in the ground state, we performed UV-vis titrations under similar conditions in CH_3CN containing 0.4% −2% DMSO. Upon addition of dicarboxylates of various chain lengths to the solution of receptor **1**, the absorption intensity, centred at 350 nm, was altered moderately without giving any appreciable red or blue shift of the absorption maximum of **1** (Figure 4 A, and Figure 7S). The flat nature of the titration curves of **1** for malonate, succinate and adipate is ascribed to the weak interaction with anions (Figure 11S). On the other hand, UV-vis spectral features of macrocycle **2** with the same guests under similar conditions were interesting. Upon successive addition of the dicarboxylates to the solution of **2,** the absorption band at 352 nm was decreased in a regular fashion without exhibiting any red or blue shift. Figure 4B, in this regard, shows the change in absorbance of **2** in the presence of glutarate in CH_3CN containing 2% DMSO. The sharp change in absorbance of **2** is consistent with the fact that the binding site of **2** is quite restricted. The conformational flexibility of the TPA core is reduced due to the presence of the macrocycle. This leads to size selectivity whereby only certain dicarboxylate anions (glutarate) fit well into the cavity with the maximum number of hydrogen bonds.

The break in the fluorescence and UV-vis titration curves (Figure 11b) for **1** and **2** at [G]/[H] = 1 is ascribed to the 1:1 stoichiometry of the [receptor⊃dicarboxylate] complexes. Job plots further confirmed the formation of 1:1 stoichiometric complexes (Figure 12S).[8]

In order to realize the binding potencies of the receptors **1** and **2** with various dicarboxylates of different chain lengths, we have determined the binding constant values from fluorescence titrations.[9] As can be seen from Table 1, the

Table 1. Binding constant values (K_a in M^{-1}) of **1**and **2** with dicarboxylates from fluorescence titration method.

Anions	Receptor **1** ($logK_a$)	Receptor **2** ($logK_a$)
Malonate	-	5.31 ± 0.22 R = 0.99
Succinate	5.35 ± 0.20 R = 0.99	5.43 ± 0.37 R = 0.98
Glutarate	6.47 ± 0.38 R = 0.98	7.04 ± 0.37 R = 0.98
Adipate	5.64 ± 0.39 R = 0.98	-
Pimelate	6.54 ± 0.55 R = 0.98	-
Suberate	6.76 ± 0.85 R = 0.98	-

'-' Binding constants were not determined due to minor change in emission during titration.

receptors bind dicarboxylates with moderate binding constant values and the selectivity trends are different. While the receptor **1** shows a preference for pimelate and suberate, receptor **2** exhibits selectivity for glutarate.

The variation found in the selectivity trend is ascribed to the unique structural features of open and macrocyclic receptors. It is worth noting that the receptor **1** showed poor selectivity for a particular dicarboxylate anion among the others under similar experimental conditions. This is presumably due to the flexible nature of the receptors for which dicarboxylates of different chain lengths can be accommodated by changing the dihedral angle around the TPA motif. In the case of macrocyclic receptor **2**, the inherent structural features of the macrocyle do not allow such conformational rotation. Therefore, only the dicarboxylates of the right sizes and shapes could be accommodated into the cavity. As a result, the glutarate anion, which has optimum size to fit into the cavity of **2**, displayed higher affinity compared to the other dicarboxylates studied. The suggested hydrogen bonded structures for **1** and

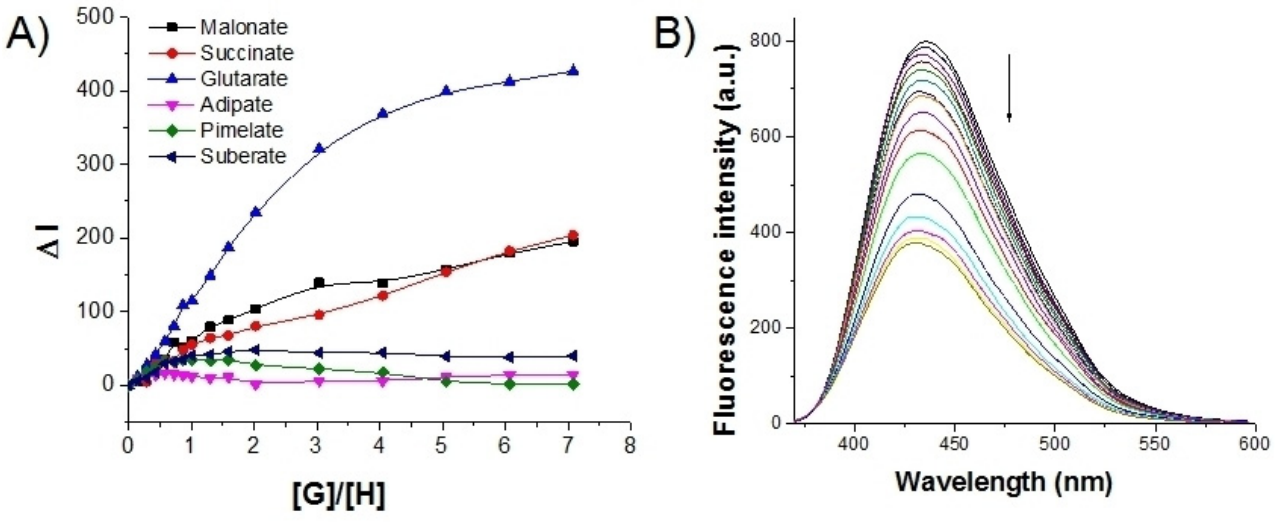

Figure 3. A) Titration curve of receptor **2** ($c = 6.23 \times 10^{-5}$ M in CH_3CN containing 2% DMSO) from fluorescence study (measured at 436 nm); B) Change in fluorescence intensity of **2** ($c = 6.23 \times 10^{-5}$ M in CH_3CN containing 2% DMSO) upon addition of glutarate (as tetrabutyl ammonium salt) ($\lambda_{max} = 436$ nm).

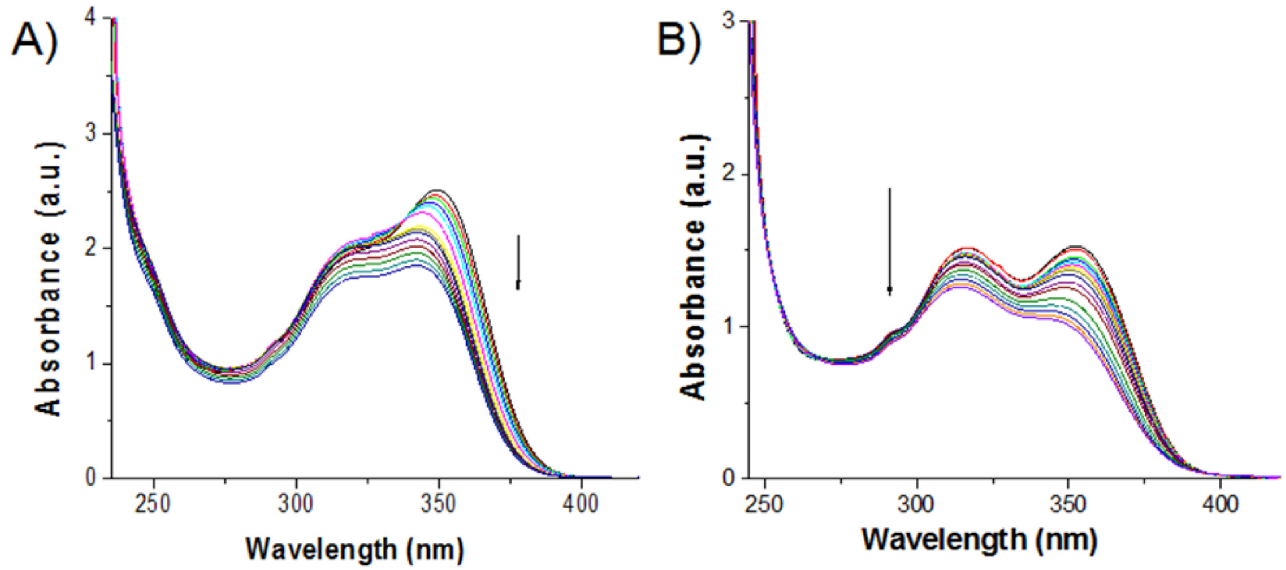

Figure 4. Change in absorbance of**1** (c = 7.66 x 10–5 M in CH_3CN containing 0.4% DMSO) and **2** ($c = 6.23 \times 10^{-5}$ M in CH_3CN containing 2% DMSO) upon gradual addition of tetrabutylammonium salt of A) suberate and B) glutarate, respectively.

2 with the dicarboxylates for [**1**.dicarboxylate]b and [**2**.dicarboxylate] complexes are represented in Figure 5.

To better understand the experimentally observed receptor behaviour (e.g., conformational mobility, selectivity trend, quenching of emission upon dicarboxylate anion binding, etc.) theoretical studies were performed. Details for all computational methods can be found in the Supporting Information. The conformational flexibility of **1** and **2** was investigated using the LM:MC conformational search method.[10] These searches were performed to gauge the overall shape and flexibility of each host and to determine whether or not the low energy structures contained well-defined binding pockets that could

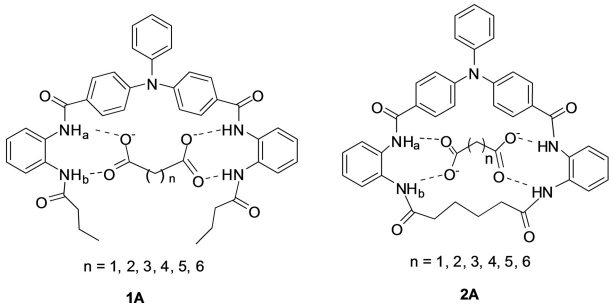

Figure 5. Schematic representation of the proposed hydrogen bonding interactions that stabilize dicarboxylate complexes of **1** and **2.**

accommodate the dicarboxylate guests for which they are intended. In all media (vacuum, GBSA chloroform and GBSA water) receptors **1** and **2** adopt triangular shaped conformers with a well-defined cavity formed by the TPA arms. The lowest energy structures for **1** and **2** in GBSA chloroform are shown in Figure 6. The amide groups on either side of the phenyl rings

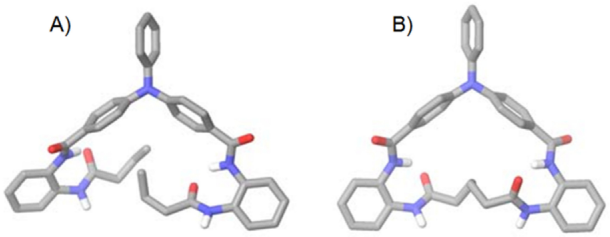

Figure 6. Lowest energy structures and hydrogen bonding patterns found for A) **1** and B) **2** in GBSA (chloroform) using the OPLS2005 force field.

calculations. However, extensive analysis of these results reveals that in most cases, the minimized structure is relatively independent of the presence or absence of solvent media. In all cases, these complexes optimize to bound structures; in the

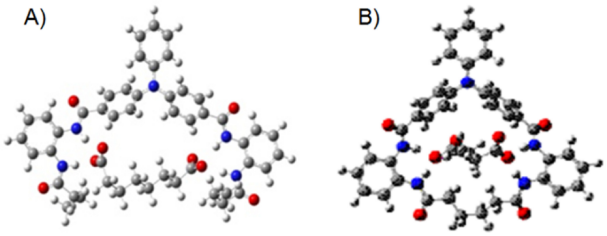

Figure 7. B3LYP/6-31G* geometry optimized structures of complexes A) [**1**⊃suberate] and B) [**2**⊃glutarate] in chloroform. Solvent effects were included in the optimization using the self-consistent reaction field (SCRF) model and the Poisson-Boltzmann (PB) solver.

Table 2. B3LYP/6-31G* binding Enthalpies (kcal/mol). Solvent effects were included in the optimization using the self-consistent reaction field (SCRF) model and the Poisson-Boltzmann (PB) solver.

Anions	Receptor 1			Receptor 2		
	ΔH (vacuum)	ΔH ($CHCl_3$)	ΔH (H_2O)	ΔH (vacuum)	ΔH ($CHCl_3$)	ΔH (H_2O)
Malonate	-120.2	-32.6	3.5	-123.9	-15.6	-2.6
Succinate	-109.5	-31.7	3.5	-98.2	-29.5	-2.2
Glutarate	-105.7	-32.6	5.8	-95.1	-23.3	-2.8
Adipate	-87.6	-30.5	15.9	-87.2	-14.5	10.4
Pimelate	-80.0	-25.9	12.5	-63.6	-21.2	6.6
Suberate	-88.7	-27.1	1.4	-67.5	-12.8	4.7

orient the NH moieties to the inside of the cavity, with N–H…H–N intramolecular distances ranging from 5.6 - 11.6 Å, providing a rough idea of the cavity size. In addition, all of the global minimum structures contain arms that seem to be controlled, in part, by the intra-arm hydrogen bonding that exists between the NH on one side of the *o*-phenylenediamine group and the C=O on the other side (Figure 15S and Table 10S).

Initially we employed force-field based conformational searching due to its computational tractability in order to understand receptor shape and flexibility. To verify the molecular mechanics results, each low energy receptor was also subjected to unrestrained quantum mechanical (QM) minimizations using the B3LYP/6-31G* methodological treatment.[11] In most cases, the overall geometry of the force-field based structures agreed with the quantum results as evidenced by the small RMSD values (Table 11S).

Quantum geometry optimizations were performed on all the [**1**.dicarboxylate] and [**2**.dicarboxylate] complexes. All dicarboxylates bind to the recetors in the *trans* conformation with significant hydrogen bonding interactions between the carboxyl end groups of the dicarboxylates and the amide NHs of each receptors. Most of the experimental work described above was performed in acetonitrile. We attempted to use the Polarizable Continuum Model (PCM) for CH_3CN as implemented in Gaussian03[12] but ran into difficulties converging the majority of cases the host adopts a triangular shape with the guest nestled into the binding pocket. Some small percentage of receptor structures can also adopt either a W-, Z- or U-shaped conformation, but in these cases a strong interaction between the guests and one of the arms persists. In what follows, we will focus on the structural results in chloroform as energetically these seem to be in the best agreement with the experimental data (vida infra).

Figure 7 A shows representative geometry optimized receptor-guest complexes for **1** with the suberate. Typically, smaller guests perturb the host less than larger guests. The structure of **1** with malonate is triangular (Figure 16S).The arms display out in the positive and negative z-direction, forming a box-like structure that surrounds the dianion. The amides of the *o*-phenylenediamine form bifurcated hydrogen bonds with the carboxylates of the guest. The structure of **1** with suberate is very similar to this but displays a noticeably larger cavity; evidence of the ability of the host to adjust to accommodate different sized guests. For **2**, all of the structures are triangular; in most structures the cavity remains relatively small, and some of the larger guests must orient perpendicular to the plane of the cavity [Figure 7B and Figure 17S].

Using Jaguar and assuming a 1:1 stoichiometry, theoretical binding enthalpies were computed and shown to vary depending on the solvent type used (Table 2.) In vacuum, all complexes of **1** and **2** displayed favorable binding interactions and showed

a strong trend that as the guests increase in size, binding energy decreases in a relatively linear fashion. Computations in chloroform were in the best agreement with the experimental binding energies shown in Table 2. In chloroform, binding enthaplies were favorable and varied with guest molecule size, but in a relatively irregular fashion reflecting the conformational changes that the hosts undergo to accommodate different sized guests. Calculations in water showed no definitive trends of any kind, with binding affinities taking on both favorable and unfavorable values, scattering about zero kcal/mol. Binding energies determined in vacuum using Gaussian 03 were in good agreement with the Jaguar results.

Conclusions

The synthesis and hydrogen bonding interactions of triphenylamine-based receptors **1** and **2** with aliphatic dicarboxylates of different chain lengths have been examined and the results have been correlated with a detailed theoretical investigation. In all the designs, *o*-phenylenediamine has been considered as the hydrogen bonding unit for complexation of the carboxylate motif. The macrocylic receptor **2** is more symmetric and efficient in selective binding and sensing of glutarate ion in the present study. The low energy structures of both the receptors in the absence of guests adopt triangular shapes with well-defined binding pockets. The receptors **1** and **2** were designed to hydrogen bond to the guests and the quantum-minimized structures reveal that the hosts are indeed interacting strongly with the guests and are flexible enough to accommodate the dicarboxylates even as they grow in size. All guests bind to hosts in the *trans* conformation with significant hydrogen bonding interactions between the carboxyl end groups of the guests and the *o*-phenylenediamine of each host.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: conformational analysis · dicarboxylate ion recognition · fluorescence quenching · glutarate anion · triphenylamine motif-based receptors

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